

NO REDUCTION BY POTASSIUM CONTAINING COAL BRIQUETTES. EFFECT OF
MINERAL MATTER CONTENT AND COAL RANK

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INTRODUCTION

Carbons and activated carbons have been proposed as reducing agents for NO removal from exhaust gases as well as for applications to vehicles and other small sources¹⁻³. The use of carbon for NO reduction could present advantages over gaseous reactants used in conventional technologies⁴. Moreover, coals could be bindered and pyrolyzed in order to obtain carbon briquettes with good mechanical strength that will resist abrasion⁵.

Recently, a method for briquette preparation and its use as NO_x reducing agent has been presented⁶. This novel manufacture method presents the advantage of using a binder agent which inherently contains potassium. Illán et al.^{7,8} found that potassium acts as catalyst of the NO-carbon reaction. In a previous paper⁹, it was found that potassium containing coal briquettes have an activity similar to that of activated carbons with potassium remaining from the preparation method although, they were not as active as activated carbon oxidized with HNO₃ and ion exchanged with potassium acetate⁸. The study⁹ was conducted using only one type of coal precursor but, as the NO-carbon reaction is a gasification reaction, it is expected that both the coal rank and the mineral matter content affect the NO reduction¹⁰.

The objective of this study is to analyze the effect of coal rank and mineral matter content in the NO reduction activity of potassium containing coal briquettes.

EXPERIMENTAL

Four coals of different rank have been selected as raw material for the briquette preparation. An anthracite (UAl), a high volatile A bituminous (A3), a high volatile C bituminous (P) and a lignite (LY). To study the effect of mineral matter content, two fractions of coal A3 with very different ash content (8% and 25%), denoted as A3 and A3' respectively, have been used. These fractions were obtained using two portions of the raw coal with different particle size ($0.71 < \phi < 1.40$ and $\phi < 0.71$ mm, respectively). To prepare the briquettes raw coals were grounded and sieved to a particle size of $0.1 < \phi < 0.2$ mm.

Commercial humic acid (liquid with a density of 1.12 g/cm³ and a potassium content of 0.049 g/cm³) has been used as binder agent for briquette preparation. The method was previously described^{6,9}. In summary, a coal sample is impregnated with a variable binder volume depending on the humic acid/coal ratio desired, mixed for 30 min, dried at 110°C, pressed (1-2 Kg/cm²) and pyrolyzed in N₂ for 2 h at 700°C. Potassium content was determined after the pyrolysis step by atomic absorption spectroscopy by AES-ICP.

After pyrolysis, a test was conducted to determine mechanical

strength of the briquettes. The impact strength test was previously described⁹. All the briquettes described in this papers have satisfactory values, independently of the humic acid/coal ratio.

The kinetics of the NO-carbon reaction were studied at atmospheric pressure in a fixed-bed flow reactor (15 mm, i.d.; ca. 300 mg sample) connected to a gas chromatograph (Hewlett Packard, Model 5890A. The reactant mixture used was: 0.5% NO in He using a 60 ml/min flow rate, which resulted in a bed residence time of 0.56 s. NO, N₂, N₂O, CO₂ and CO were analyzed using a Porapak Q 80/100 column and a thermal conductivity detector. Briquettes were ground to < 1.5 mm to introduce them in the microreactor.

Two types of experiments were performed: i) a temperature programmed reaction (TPR) at a linear heating rate of 5°C/min up to a maximum temperature of 900°C; and ii) an isothermal reactions at 300, 400, 500 and 600°C for 120 minutes. The samples were treated in helium at 50°C/min, up to 900°C for 10 minutes prior the reaction. In case i), the temperature is lowered to ambient temperature and He replaced by the reactant mixture. In case ii), the temperature is lowered to the desired level and the isothermal experiment is initiated by substituting He by the NO/He mixture. The reaction products were monitored in both cases, thus allowing detailed oxygen and nitrogen balances to be determined.

RESULTS AND DISCUSSION

Table 1 presents the results for sample preparation, consisting of coal precursor, humic acid to coal ratio (HA/C), yields of the pyrolysis process and sample nomenclature including final potassium content. It is interesting to note that samples prepared, with the same HA/C (1.20), using the different coal precursors present a very different potassium content which is higher as coal rank decreases. This fact must be due to two phenomena, the increase in weight lost during pyrolysis from the anthracite to the lignite, as observed in the values of pyrolysis yield (Table 1) and the higher oxygen surface groups as coal rank decreases¹¹, that are mainly responsible for potassium anchorage¹².

For a fixed coal, an increase in HA/C produces an increase in potassium content up to a limit value, this could be observed in the series prepared from coals P and LY (Table 1). For coal P, an increase from 0.8 to 1.2 in HA/C only produces a 20% increase in potassium content while from 0.4 to 0.8 it increases in 100%. The specific activity (per gram of potassium) decreases, for a given coal precursor, with increasing potassium content. This behaviour was previously observed and explained for potassium impregnated activated carbons⁸.

To study the effect of coal rank, briquettes with similar potassium contents have been prepared from coals UA1, P and LY. Figure 1 presents the results of specific activity determined at steady state conditions, at different temperatures, as a function of percentage of fixed carbon in the coal precursor. It is clearly observed a decrease in activity as the coal rank increases. Briquettes prepared from lignite (LY) has a much higher activity. It may be observed that the same value is found for sample LY-1.9 at 400°C and for sample P-1.5 at 600°C. A reduction of 200°C in the process temperature is very important for a practical point of view. It is also interesting to note that the ash content of coal LY is very low (0.5 wt%) in comparison to UA1 (7.0 wt%) or P (16.7 wt%). Both low rank and low ash content could be responsible for

the high activity, as we will discuss later. Sample LY-1.9 has an activity as high as that of an activated carbon, oxidized with HNO_3 and ion-exchanged with potassium acetate¹³. The behaviour of both samples for NO reduction in the temperature range studied (300-600°C) is very similar. These results confirm that, if very reactive low rank coals are used as precursors, the briquetting process can produce very active samples, with the advantage of higher mechanical strength and in a very simpler procedure.

Figure 2 shows the activity plots for briquettes A3-4.7 and A3'-3.6. As already mentioned in the experimental section, these samples were prepared from two portions of coal A3 containing different ash content. At 600°C the behaviour is not very different for the two samples although, at steady state conditions the activity level is more constant for the sample prepared with low ash content coal. At 500°C, the difference is dramatic. Sample A3'-3.6 very much deactivates presenting a very low activity at steady state conditions.

To explain these results, the analysis of reaction products, mainly N_2O , N_2 , NO, CO_2 and CO, during TPR experiments are presented in Figures 3 and 4. Similar results were obtained for potassium containing activated carbons⁸. The profiles can be described as follows:

i) An initial period from 100 to 300°C with NO uptake reaching a maximum about 150°C. In this zone N_2O and N_2 are the only products.

ii) A second period from 300 to 600 °C, where NO reduction activity increases with temperature. In this zone N_2 and CO_2 are the main products.

iii) Above 600°C, N_2 becomes constant, the 100% NO reduction is reached and CO begins to evolve being the majority product at about 800°C. The CO appearance coincides with the complete disappearance of NO.

However, an important difference is observed in these plots in comparison to those of potassium containing activated carbons. The CO_2 evolution reaches a maximum at 620-650°C that is typical of most of the briquette samples⁹.

For potassium containing activated carbons⁸, an excess CO_2 in relation to N_2 (both the main reaction products at this temperature range) was observed forming a broad band but, no single peak appeared. In a previous study⁹, the CO_2 peak, appearing in the TPR of coal briquettes has been attributed to K_2CO_3 decomposition, considering the temperature range of appearance. The area under the peak allows to calculate the carbonated potassium during TPR experiment. This portion of the metal will be inactive as catalyst for the reaction⁸. The results in Figures 3 and 4 explain the large difference in activity at 500°C for samples A3-4.7 and A3'-3.6. For the second one (Figure 4) an 88% of the catalyst is in the carbonated form while only 25% for the former one (Figure 3). At 600°C, the K_2CO_3 decomposition starts and the activity is very similar for both samples.

At present, it is not probed the origin of the negative effect of mineral matter, present in the raw coal, that produces an increase in the K_2CO_3 formation. The hypothesis that is being investigated,

it is that mineral matter acts as a sink for potassium, producing a lower dispersion and consequently larger particles that will be easier carbonated in the reaction conditions since most part of the catalyst is not in contact with the carbon substrate.

CONCLUSIONS

NO reduction activity of potassium containing coal briquettes depends on coal precursor rank. Regarding samples with similar potassium content the activity increases with decreasing coal rank. Coal rank also affects potassium content of the briquettes. Using a similar humic acid to coal ratio the lower the coal rank the higher the potassium content. Briquettes prepared from low rank coals are as active as potassium ion-exchanged activated carbons which need a much more complicated preparation method. Mineral matter in the coal precursor produces deactivation of potassium catalyst, favoring the K_2CO_3 formation in reaction conditions.

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TABLE 1. Briquette preparation

Coal precursor	Humic acid/ coal ratio	pyrolysis yield (%)	Briquette nomenclature
UA1	1.20	88.1	UA1-1.3
A3	1.20	72.0	A3-4.7
A3'	1.20	---	A3'-3.6
P	0.40	---	P-1.5
P	0.80	---	P-3.2
P	1.20	65.2	P-3.9
LY	0.25	52.1	LY-1.9
LY	0.78	53.4	LY-6.0
LY	1.20	53.4	LY-7.2

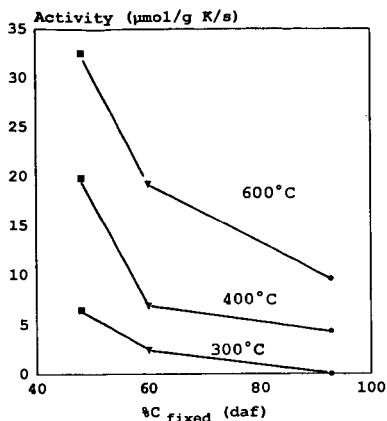


Figure 1. Briquette specific activity for NO reduction versus fixed carbon of coal precursors. (*UA1-1.3, ▼P-1.5, ■LY-1.9)

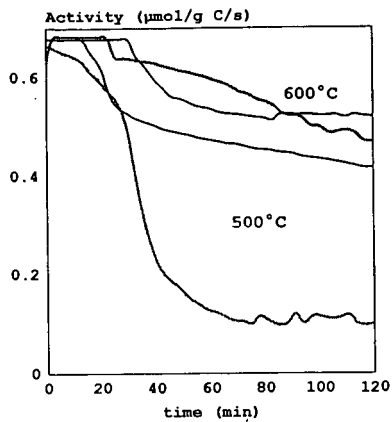


Figure 2. NO reduction activity curves. (—A3-4.7, —A3'-3.6)

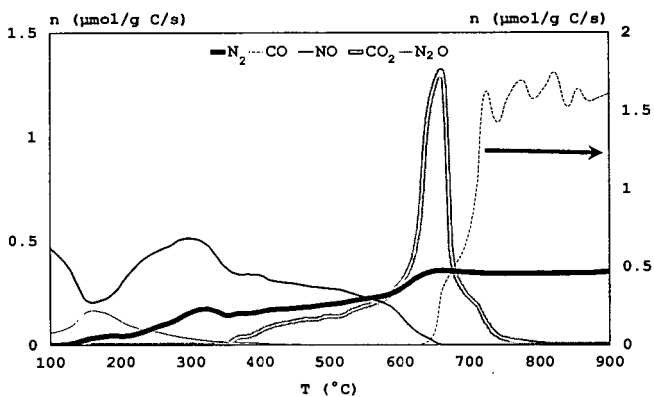


Figure 3. TPR gas composition profiles for briquette A3'-3.6.

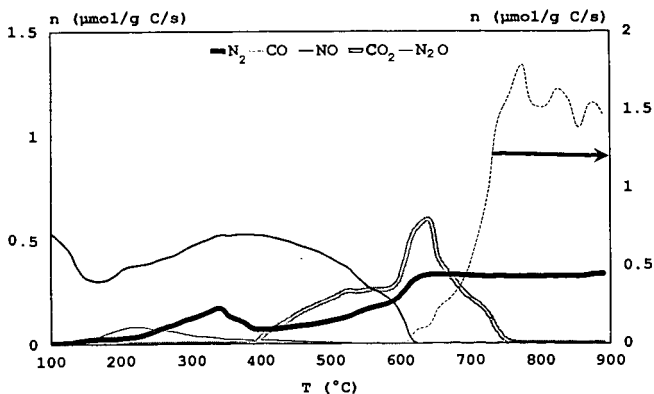


Figure 4. TPR gas composition profiles for briquette A3-4.7.